Indian Journal of Chemistry
Vol. 14A, November 1976, pp. 888-891

Expression for the Formation Constant of a 1:1 Complex in Terms of the Area under the Mole Ratio Curve*

H. PARASURAMA IYER & P. S. RAMANATHAN
Analytical Chemistry Division, Bhabha Atomic Research Centre, Trombay, Bombay 400085

Received 19 *November* 1975; *accepted* 26 *March* 1976

A mathematical expression for the formation constant (K) of a 1:1 complex has been derived in terms of the area (D) under the mole ratio curve up to any arbitrarily chosen value (C_A°) of the ligand concentration (C_A). The evaluation of K using the mole ratio curve for any given metal concentration (C_M), however, requires a knowledge of the fraction of the metal complexed ($p^\circ = C^\circ/C_M$ where C° is the concentration of the complex formed when $C_A = C_A^\circ$). It has been shown that D varies as $1/K$ for 1:1 complexes if C_M and P° are constant in all the cases. The expression for D has been transformed into two other linear equations which can be put to practical use. In these two equations D_C/C_M^2 and D_{sp}/C_M^2 respectively turn out to be linear functions of $1/C_M$ when p° is fixed. D_C and D_{sp} represent the area under the curve when the concentration of the complex (C) and optical density (E) are respectively chosen as the ordinate. It has also been shown that the function J_{sp}/C_M (where $J_{sp} = E^\circ.C_A^\circ - D_{sp}$) is linearly related to E° (the values of E chosen from mole ratio curves drawn for different C_M values in such a way that E/C_M is constant) when p° is fixed. Using the data obtained from (a) a set of theoretical mole ratio curves and (b) Cu-ethylenediamine system at pH 4·5, the validity and practical utility of the linear equations (to arrive at K and ϵ values) have been demonstrated.

THE mole ratio method[1,2] has been wi de ly used to arrive at the composition of strong complexes formed in solution. As the shape of the mole ratio curve depends upon (a) C_M, the total concentration of the metal ion, (b) K, the conditional formation constant and (c) the composition of the complex formed, the area D of the figure (e.g. OPQ in Fig. 1) bounded by the mole ratio curve, the abscissa and the ordinate at any chosen ligand concentration (C_A°) must be related to these factors by appropriate mathematical expressions.

The present paper deals with the derivation of such a mathematical expression, applicable for systems in which a 1:1 complex forms exclusively in all the solutions.

Derivation of the Relation Connecting D and K

A section of the mole ratio curve of a 1:1 complex (with $K=10^2$) is given in Fig. 1. D_c, the area of OPQ when C, the concentration of the complex is chosen as ordinate is given by Eq. (1).

$$D_c = C^\circ.C_A^\circ - \text{Area } J_c = C^\circ.C_A^\circ - \int_0^{C^\circ} C_A.\, dC \qquad \ldots(1)$$

where, C° and C_A° are the values of C and C_A respectively corresponding to any point P, chosen arbitrarily on the mole ratio curve.

By rearranging the familiar equation for K one gets

$$C_A = C + C/K(C_M - C) \qquad \ldots(2)$$

Substituting this value of C_A in Eq. (1) and by further manipulations [after introducing the variable $X=(C_M-C)$] one gets

$$J_c = C^{\circ 2}/2 - C^\circ/K - (C_M/K)\ln[(C_M - C^\circ)/C_M] \qquad \ldots(3)$$

Using this value of J_c it is easy to show that

$$D_c = (p^{\circ 2}C_M^2/2) + (C_M/K)[(p^\circ/(1-p^\circ)) + \ln(1-p^\circ)] \qquad \ldots(4)$$

where p° is the fraction of the metal involved in complex formation. Eq. (4) shows that D_c varies linearly with $1/K$ for 1:1 complexes, if C_M and p° are fixed. The second term on the right hand side of Eq. (4) represents the difference between the area D_c (found for the complex under investigation) and $p^{\circ 2}C_M^2/2$, the value expected for a very stable complex (selecting the same C_M and p° values for both cases).

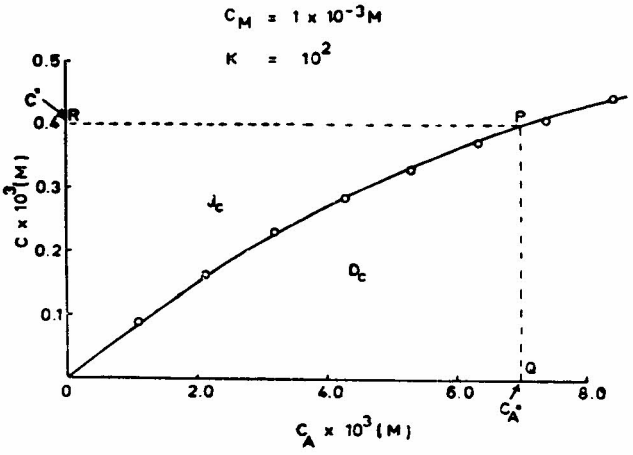

Fig. 1 — Mole ratio curve of a 1:1 complex [$C_M = 1{\cdot}0 \times 10^{-3} M$; $K = 1{\cdot}0 \times 10^2$]

*Presented in part at the Convention of Chemists, held at Madurai, during December 1974.

From Eq. (4) one obtains the following expression for K.

$$K=C_M[(p^\circ/(1-p^\circ)+\ln(1-p^\circ)]/[D_c-(p^{\circ 2}C_M^2/2)] \quad ...(5)$$

Eq. (4) can be rewritten as

$$D_c/C_M^2=(p^{\circ 2}/2)+(1/KC_M)[p^\circ/(1-p^\circ)+\ln(1-p^\circ)] \quad ...(6)$$

It is obvious that a plot of D_c/C_M^2 vs $1/C_M$, drawn for any constant p° value, will be linear.

When spectrophotometry is employed for investigation and E values contributed by the complex are plotted against C_A to obtain the mole ratio curve, one gets the following expression for D_{sp}/C_M^2.

$$D_{sp}/C_M^2=(E^{\circ 2}/2\epsilon C_M^2)+(\epsilon/KC_M)\left[\left\{\frac{E^\circ/\epsilon C_M}{1-(E^\circ/\epsilon C_M)}\right\}+\ln(1-E^\circ/\epsilon C_M\right] \quad ...(7)$$

$D_{sp}=\epsilon D_c$ and $E^\circ=\epsilon C^\circ$, where ϵ is the molar extinction coefficient of the complex. If one plots D_{sp}/C_M^2 against $1/C_M$ for constant E°/C_M values (by selecting points from mole ratio curves with different C_M values) a linear curve will be obtained. From the intercept and slope of the linear plot ϵ and K can be computed.

It is to be pointed out that ϵ and K can also be arrived at from the area $J_{sp}(=\epsilon J_c)$. Starting from Eq. (3) one can show that

$$J_{sp}/C_M=(E^\circ/2\epsilon C_M).E^\circ-E^\circ/C_MK-(\epsilon/K)\ln(1-E^\circ/\epsilon C_M) \quad ...(8)$$

From mole ratio plots corresponding to different C_M values one can compute values of J_{sp} (corresponding to constant E°/C_M values). A plot of J_{sp}/C_M against E° will be a straight line. ϵ and K can be calculated from the slope and intercept respectively of this straight line.

Validity of Eqs. (6), (7) and (8)

Curves I to IV in Fig. 2 represent the theoretical mole ratio curves of a 1:1 complex with $K=10^2$. They have been drawn for different C_M values.

Case 1: *Plot of* D_c/C_M^2 *vs* $1/C_M$ — The points a, b, c and d on curves I to IV respectively correspond to a constant p° value of 0·2. The area D_c under each curve, up to the point chosen on the curve, is determined. The value of D_c/C_M^2 is then computed for each curve and plotted against $1/C_M$, when the linear curve (a) in Fig. 3 is obtained, as expected from Eq. (6). Curve (b) in Fig. 3, which is similar to curve (a), has been drawn for $p^\circ=0{\cdot}3$. The data needed for this have been obtained by selecting points e, f, g and h on curves I to IV (Fig. 2) respectively.

Case 2: *Plot of* D_{sp}/C_M^2 *vs* $1/C_M$ — The molar extinction coefficient ϵ has been taken to be equal to 1000 for the 1:1 complex under investigation as this will make the ordinate in Fig. 2 directly represent E. The points a, b, c and d in curves I to IV will, in this case, correspond to those with the constant E°/C_M value of 200, while e, f, g and h will refer to the constant E°/C_M value of 300. By appropriate choice of the scale for the ordinate, curves (a) and (b) in Fig. 3 respectively have been made to represent the variation of D_{sp}/C_M^2 as a function of $1/C_M$ in the above two cases.

Case 3: *Plot of* J_{sp}/C_M *vs* E° — The linear curves (a) and (b) in Fig. 4 represent the variation of J_{sp}/C_M as a function of E° for constant E°/C_M values of 200 and 300 respectively.

The data needed to plot all the curves mentioned above are given in Table 1. The linear nature of the different curves in Figs. 3 and 4 confirm the

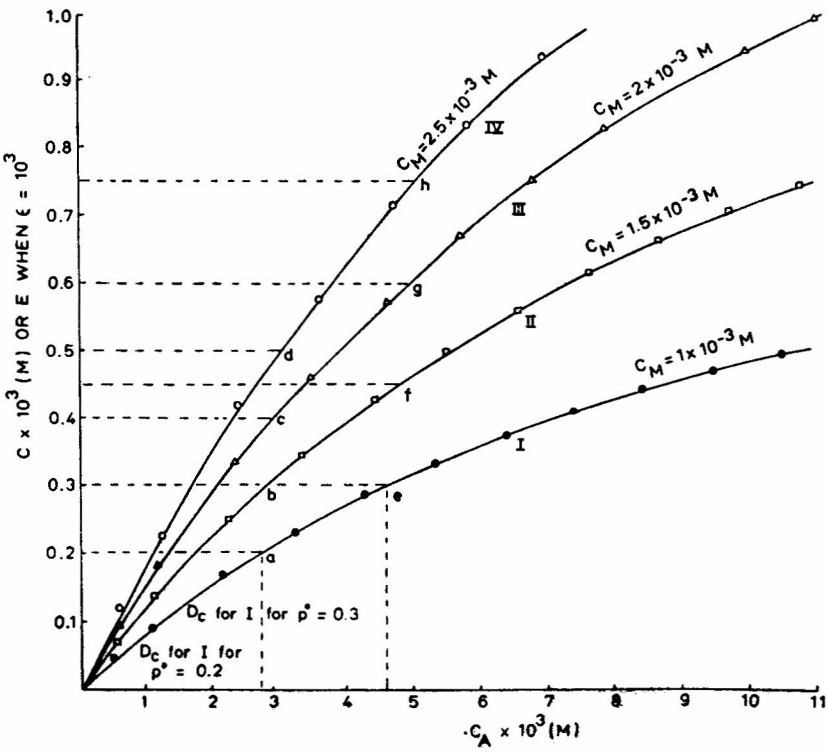

Fig. 2 — Theoretical mole ratio curves for a 1:1 complex with $K=10^2$ for different C_M values

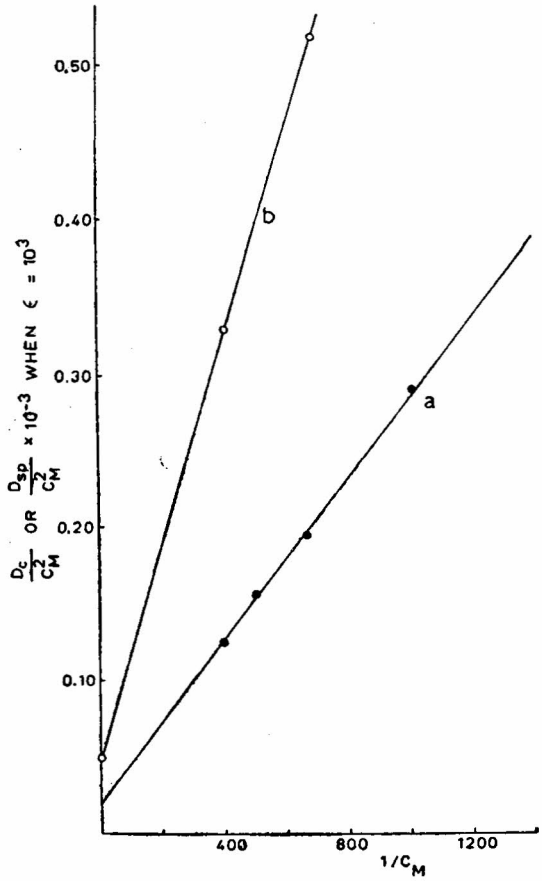

Fig. 3 — Plots of (a) D_C/C_M^2 vs $1/C_M$ for constant p° values and (b) D_{sp}/C_M^2 vs $1/C_M$ for constant E°/C_M values [Curve (a) $p^\circ = 0{\cdot}2$ and $E^\circ/C_M = 200$; and curve (b) $p^\circ = 0{\cdot}3$ and $E^\circ/C_M = 300$]

validity of the Eqs. (6), (7) and (8). The slopes and intercepts found for the linear plots were compared with those expected from the corresponding equations. Good agreement was found between the expected and observed values which further proved the validity of the three equations.

Evidently, Eqs. (7) and (8) can also be applied in the appropriate form for those cases in which

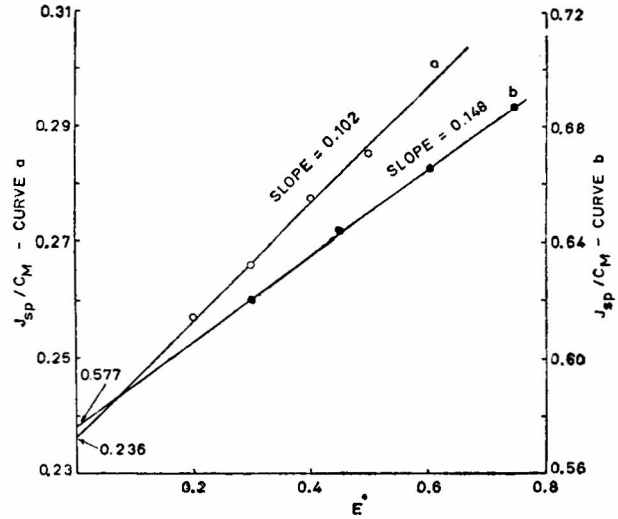

Fig. 4 — Plots of J_{sp}/C_M vs E° for constant E°/C_M values [Curve (a) $E^\circ/C_M = 200$; curve (b) $E^\circ/C_M = 300$]

any other physico-chemical property proportional to the concentration of the complex is utilized to study complex formation.

Practical Applications

It is obvious that Eqs. (6) to (8) will not deserve consideration to study systems involving strong and moderately strong 1:1 complexes, as these cases can be handled by less cumbersome procedures. However, these equations will be quite useful to arrive at K and ϵ of 1:1 complexes which are so dissociating that colour saturation cannot be obtained under the experimental conditions (or can be obtained only with very high C_A/C_M values).

Taking the 1:1 complex formed between Cu(II) and ethylenediamine at *p*H 4·5 as a practical example of a system exhibiting reasonably high dissociation, the molar ratio curves were obtained at 650 nm for different C_M values ($0{\cdot}01M$, $0{\cdot}015M$, $0{\cdot}02M$ and $0{\cdot}025M$). Linear curves connecting D_{sp}/C_M^2 and $1/C_M$ were then drawn for the constant E°/C_M values of 10, 15 and 20. From the intercepts and slopes respectively of all these linear curves,

TABLE 1 — DATA FOR PLOTTING THE LINEAR CURVES IN FIGS. 3 AND 4

Curve No. in Fig. 2	$C_M \times 10^3$ (M)	Exptl point chosen	$C^\circ \times 10^3$ (M) or E°	$Dc \times 10^6$ or $D_{sp} \times 10^3$	$(Dc/C_M^2) \times 10^3$ or D_{sp}/C_M^2	$J_{sp} \times 10^3$	J_{sp}/C_M	$1/C_M$
(A) CONSTANT VALUE OF p° CHOSEN = 0·2; CONSTANT VALUE OF E°/C_M = 200; ϵ = 1000								
I	1·0	a	0·2	0·2929	292·9	0·2571	0·2571	1000
II	1·5	b	0·3	0·4407	195·9	0·3993	0·2662	667
III	2·0	c	0·4	0·6247	156·2	0·5553	0·2773	500
IV	2·5	d	0·5	0·7876	126·0	0·7124	0·2850	400
(B) CONSTANT VALUE OF p° CHOSEN = 0·3; CONSTANT VALUE OF E°/C_M = 300; ϵ = 1000								
I	1·0	e	0·3	0·7592	759·2	0·6208	0·6208	1000
II	1·5	f	0·45	1·1717	520·8	0·9653	0·6435	667
III	2·0	g	0·6	1·6072	401·8	1·3328	0·6664	500
IV	2·5	h	0·75	2·0689	331·0	1·7186	0·6874	400

TABLE 2 — K AND ε VALUES OF Cu-ETHYLENEDIAMINE COMPLEX, ARRIVED AT USING EQ. (7)

[pH = 4·5]

$E°/C_M$	ε from intercept	ϵ^*_{sat}	log K from slope	log $K^\dagger_{sat}$
10	35	33	2·29	2·39
15	34		2·40	
20	33		2·42	

*Average value calculated from colour saturation experiments carried out at higher pH values.

†Average value calculated using $E_{saturation}$ and several E values chosen from mole ratio curves drawn at pH 4·5.

TABLE 3 — K AND ε VALUES OF Ti-SULPHOSALICYLIC ACID SYSTEM, ARRIVED AT USING EQ. (7)

[Acidity = 1·87N (sulphuric acid medium)]

$E°/C_M$	Intercept	ε from intercept	Slope	K from slope	log $K^\dagger_{calc.}$
25	60	5·2	1·67	*	2·35
40	60	13·3	4·44	*	2·12
50	60	20·8	6·63	*	1·97

*Cannot be calculated as $(1-E°/\epsilon C_M)$ turns out to be negative.

†log K values calculated from two points on the same mole ratio curve by conventional procedure.

values of ε and K were arrived at. These values are compared, in Table 2, with those arrived at by other methods. The reasonable agreement between the two sets of results can be taken to confirm the practical utility and reliability of the new method proposed.

Application of this new approach to the highly dissociating system of Ti(IV)-sulphosalicylic acid (at 1·87N acidity)[3] gave linear plots as expected. However, the ε values arrived at for different $E°/C_M$ values did not exhibit constancy. Even the values of ε obtained were found to be inadmissible (Table 3). The K values could not be calculated from the slope, as $(1-E°/\epsilon C_M)$ turned out to be negative in all the cases. In the opinion of the authors, obtaining the sets of linear curves mentioned earlier in any system is an indirect evidence for the predominant formation of coloured complex species with 1:1 composition. Lack of constancy and/or inadmissibility of the ε and K values arrived at for different $E°/C_M$ values can, therefore, be taken as an indication of the existence of perturbing side equilibria [e.g. (a) More than one complex with composition 1:1 and with comparable stability may be forming in comparable concentrations in the different solutions or (b) traces of coloured species with different stoichiometry, stability and spectra may be forming along with the predominant 1:1 species]. Evidences for the existence of multiple equilibria in Ti(IV)-sulphosalicylic acid system has been provided in some earlier communications[3,4]. The greater spread in the log $K_{calc.}$ values, arrived at by conventional procedure, is also worth noting (Table 3).

The new method proposed in this paper can, therefore, be fruitfully utilized (a) to arrive at ε and K in dissociating systems in which a single 1:1 complex forms exclusively in all the solutions under the experimental conditions, (b) to confirm indirectly the predominant formation of a 1:1 complex (based on the linear curves obtained by the different procedures) and (c) to function as a pointer to reveal the presence of multiple equilibria (based on the inconsistent and/or inadmissible ε and K values obtained for different $E°/C_M$ values).

The equations arrived at are similar to that proposed by Benesi and Hildebrand[5]. They are, however, exact and do not involve any approximation similar to that employed in the latter.

Acknowledgement

The authors are grateful to Dr M. Sankar Das and Dr Ch. Venkateswarlu for their valuable criticisms during the preparation of this manuscript.

References

1. MILNER, T., *Z. analyt. Chem.*, **113** (1938), 83.
2. YOE, J. H. & JONES, A. L., *Ind. Engng Chem. Anal. Edn*, **16** (1944), 111.
3. ATHAVALE, V. T., KRISHNAN, C. V., RAMANATHAN, P. S. & VENKATESWARLU, CH., *Indian J. Chem.*, **7** (1969), 1040.
4. MAHADEVAN, N., SATHE, R. M. & VENKATESWARLU, CH., *J. inorg. nucl. Chem.*, **25** (1963), 1005.
5. BENESI, H. A. & HILDEBRAND, J. H., *J. Am. chem. Soc.*, **71** (1949), 2703.